Experimental Section

Most of the equipment and techniques have been described in preceding papers.[4,9]

Photolysis of 1 in Alcohols. A solution of 1 (5.0 g, 0.043 mol) in alcohol (0.5 mol) was irradiated by using a low-pressure mercury lamp, with stirring and cooling at 0 °C, until the evolution of nitrogen was no longer observed. In the case of thermolysis, a solution of 1 (1.15 g, 0.01 mol) in alcohol (0.2 mol) was heated at 110 °C in a sealed tube for 8 h. The excess substrate and the volatile product, aldehyde or ketone, were trapped in a dry ice–methanol bath under reduced pressure. The trapped solution was added to a 2,4-dinitrophenylhydrazine solution, and the hydrazone was isolated. The residue was analyzed by VPC. The IR and the NMR data of **4B**, **4C**, **4D**, **4G**, **5B**, **5C**, **5D**, and **5G** were reported previously.[3] The insertion products (**4A**, **4F$_1$**, **4F$_2$**) and **5F** displayed strong absorptions in the 3260–3360- and 1700–1730-cm^{-1} regions due to the NH groups and the ester C=O groups, respectively.

N-Methoxyurethane (4A): NMR (CCl_4) δ 1.29 (t, 3, ester CH_3), 3.65 (s, 3, CH_3), 4.15 (q, 2, CH_2), 8.25 (brd s, 1, NH). Anal. Calcd for $C_4H_9O_3N$: C, 40.33; H, 7.62; N, 11.76. Found: C, 40.23; H, 7.56; N, 11.69.

N-Isobutoxyurethane (**4F$_1$**): NMR (CCl_4) δ 0.94 (d, 6, 2 CH_3), 1.60–2.15 (m, 1, CH), 2.29 (t, 3, ester CH_3), 3.57 (d, 2, CH_2), 4.14 (q, 2, ester CH_2), 7.85 (brd s, 1, NH). Anal. Calcd for $C_7H_{15}O_3N$: C, 52.15; H, 9.38; N, 8.69. Found: C, 52.07; H, 9.25; N, 8.76.

N-(1,1-Dimethyl-2-hydroxyethyl)urethane (**4F$_2$**): NMR (CCl_4) δ 1.25 (s, 6, 2 CH_3), 1.25 (t, 3, ester CH_3), 3.46 (s, 2, CH_2), 3.46 (s, 1, OH), 4.01 (q, 2, ester CH_2), 4.90 (brd s, 1, NH). Anal. Found: C, 52.11; H, 9.28; N, 8.80.

N-(2-Methyl-1-isobutoxypropyl)urethane (**5F**): NMR (CCl_4) δ 0.92 (d, 12, 4 CH_3), 1.29 (t, 3, ester CH_3), 1.74 (mult, 2, CH), 3.57 (d, 2, CH_2), 4.15 (q, 2, ester CH_2), 4.55 (mult, 1, NCH), 5.32 (brd s, 1, NH). Anal. Calcd for $C_{11}H_{23}O_3N$: C, 60.80; H, 10.67; N, 6.45. Found: C, 60.76; H, 10.59; N, 6.52.

Photolysis of 1 in a Substrate Mixture. A solution of 1 (5.0 g, 0.043 mol) in a substrate mixture (each 0.25 mol) was irradiated internally as has been described above. Then the reaction mixture was treated as mentioned above.

Acknowledgment. The authors are particularly indebted to Mr. Masao Inagaki of the College of General Education, Osaka University, for help in the preparation of this paper and for many useful suggestions.

Registry No. 1, 817-87-8; **2**, 2655-26-7; **4A**, 3871-28-1; **4B**, 38483-42-0; **4C**, 38483-43-1; **4D**, 38483-44-2; **4E**, 70084-52-5; **4F$_1$**, 63767-49-7; **4F$_2$**, 70084-53-6; **4G**, 38483-45-3; **5A**, 6781-01-7; **5B**, 1471-64-3; **5C**, 38542-87-9; **5D**, 38483-40-8; **5E**, 70084-54-7; **5F**, 70084-55-8; **5G**, 63767-45-3; methanol, 67-56-1; ethanol, 64-17-5; propanol, 71-23-8; butanol, 21-36-3; 2-propanol, 67-63-0; 2-methyl-1-propanol, 78-83-1; 3-methyl-1-butanol, 123-51-3; butyl ether, 142-96-1; cyclohexane, 110-82-7; ethyl cyclohexylcarbamate, 1541-19-1.

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(9) Shingaki, T.; Inagaki, M.; Takebayashi, M.; Lwowski, W. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3567.

A New Synthesis of the Isophosphindoline System[1]

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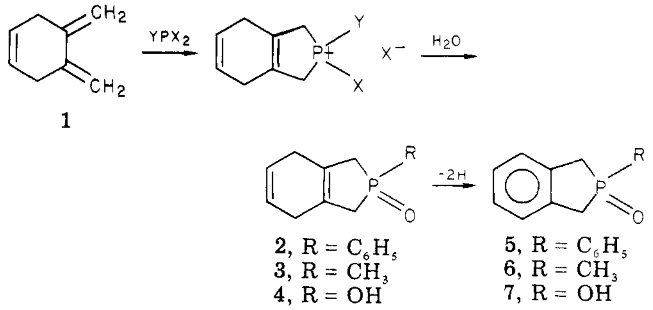
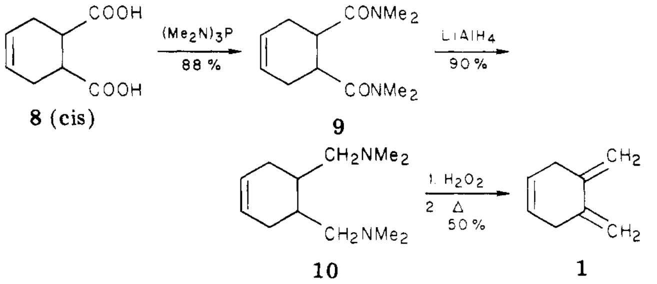
Received February 20, 1979

The isophosphindoline system was first constructed in the pioneering work of Mann and associates in 1954,[2] who later found that the *P*-phenyl derivative had especially valuable metal-complexing abilities.[3] Mann's synthesis of this ring system employed the principle of cyclization of an ortho-disubstituted benzene with a phosphorus compound, and all but one[4] of several subsequent syntheses[5] have made use of this principle with various reagents. The published methods have limited scope, however, and the number of known derivatives of this ring system remains quite small. We have now devised an entirely different approach to the isophosphindoline system which provides some variety in the phosphorus functionality produced (phosphine oxide or phosphinic acid) and for the former, in the carbon substituent on phosphorus.

Scheme I



Scheme II



Our approach involves the creation of the phosphorus-containing ring before development of the aromatic system and depends on the versatile McCormack cycloaddition reaction[6] to construct the requisite molecular framework (Scheme I). Many P(III) halides are known to participate in such cycloadditions, and in the present study we have used two phosphorus dihalides, CH_3PCl_2 and $C_6H_5PBr_2$, as well as PBr_3. Diene 1 has never before been used in a McCormack cycloaddition, but it responds exceptionally well to the usual mild conditions (standing at room temperature for several days) and leads to excellent yields of solid adducts. These were hydrolyzed without isolation to provide the new phospholene oxides **2** (85%) and **3** (92%) and the phosphinic acid **4** (78%). The value of our synthesis depends, of course, on the availability of known[7] diene 1, and in Scheme II is outlined

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(1) Supported by NSF Grant CHE77-17876 and ARO Grant DAAG29-76-G-0267.

(2) (a) F. G. Mann, I. T. Millar, and F. H. C. Stewart, *J. Chem. Soc.*, 2819 (1954); (b) F. G. Mann and F. H. C. Stewart, *ibid.*, 2832 (1954); (c) F. G. Mann, I. T. Millar, and H. R. Watson, *ibid.*, 2516 (1958).

(3) F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, and Bismuth", Wiley-Interscience, New York, N.Y., 1970, pp 70–71.

(4) J. M. Holland and D. W. Jones, *J. Chem. Soc., Perkin Trans. 1*, 927 (1973); the *o*-quinonoid tautomer of 1,2-diphenylbenzocyclobutene was employed as a diene in cycloaddition with $C_6H_5PCl_2$, generating 1,2,3-triphenylisophosphindoline 1-oxide.

(5) For leading references, see ref 2 and S. D. Venkataramu, G. D. Macdonell, W. R. Purdum, M. El-Deek, and K. D. Berlin, *Chem. Rev.*, **77**, 121 (1977).

(6) W. B. McCormack, U.S. Patents 2 663 736 and 2 663 737 (1953). Reviewed by L. D. Quin, "1,4-Cycloaddition Reactions", J. Hamer, Ed., Academic Press, New York, N.Y., 1967, Chapter 3.

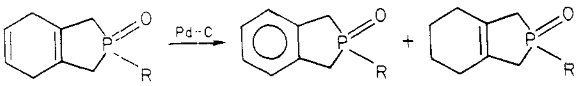
(7) W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

0022-3263/79/1944-2587$01.00/0

a new and efficient method for its synthesis. The scheme is similar to one we have reported for 1,2-dimethylenecyclohexane.[8]

The aromatization of the intermediate phospholene oxides is easily accomplished by refluxing with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene. Yields of the three easily crystallized products **5**–**7** were 47, 66, and 91%, respectively. The two phosphine oxides are quite hygroscopic, however, and the *P*-methyl compound (**6**) tenaciously held 1 mol of water. This behavior had been noted previously for the phenyl compound.[2c,9] The phosphinic acid, on the other hand, is a nonhygroscopic, easily isolated solid. While its NMR spectrum matched that reported previously,[10] the melting point of our analytically pure sample was several degrees higher (156–158 °C, compared to 142–148 °C).

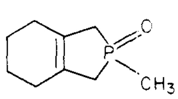
The aromatization of **3** and **4** has also been accomplished with Pd-C in refluxing cumene. While the yields are high (80–85%), the products are contaminated with as much as 15–30% of the corresponding hexahydroisophosphindole derivative (**11** and **12**, respectively) from transfer of hydrogen to the starting tetrahydro derivatives. These byproducts are difficult to remove, and this dehydrogenation route is generally less satisfactory than that employing DDQ.



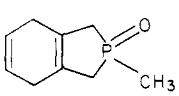
11, R = CH_3
12, R = OH

^{13}C NMR data for some of the compounds are given in Table I. The spectra lent themselves to ready interpretation, except where intermingling of two sets of aromatic signals occurred (**2** and **5**). The dihydrophosphindoline derivatives **3** and **4** displayed the uncommon feature of ^{31}P coupling through four bonds, splitting C-5,6 in each to doublets of $J = 1.8$ Hz. The effect was absent in the aromatized system.

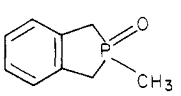
The compounds allow a consideration of the influence of unsaturation in the six-membered ring on the ^{31}P NMR shift. As seen in the *P*-methyl series below for D_2O solution, the shifts are rather similar but incorporation of the double bond at the 3,4 position into an aromatic system does have the apparent effect of modest deshielding of the P atom.



11, $\delta(^{31}P)$ +68.5



3, $\delta(^{31}P)$ +68.9



6, $\delta(^{31}P)$ +73.3

Experimental Section[11]

***cis*-*N*,*N*,*N'*,*N'*-Tetramethyl-4-cyclohexene-1,2-dicarboxamide (9).**[13] To a suspension of 4-cyclohexene-*cis*-1,2-dicarboxylic acid (170.1 g, 1.0 mol) in benzene (500 mL) was added hexamethylphosphorous triamide[12] (163.2 g, 1.0 mol) at a rate that maintained reflux of the reaction mixture. The resulting cloudy solution was allowed to cool to room temperature and a saturated $NaHCO_3$ solution (400 mL) was added. The layers were separated and the aqueous layer was extracted with methylene chloride (four 150-mL portions). The organic solutions were combined, dried ($MgSO_4$), and concentrated to give a clear, colorless oil which solidified to a white solid. After the solid was washed with hexane, 196.4 g (88%) of diamide **9** was obtained; mp 63–69 °C. Recrystallization from ether at −78 °C gave white needles: mp 72–73 °C; IR (neat) 1630 cm^{-1} ($\nu_{C=O}$); ^1H NMR (CCl_4) δ 1.84–3.36 (m, 18 H, including br s at 2.96), 5.68 (s, 2 H, C=CH).

Anal. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.25; H, 8.99; N, 12.49. Found: C, 64.37; H, 9.01; N, 12.23.

***cis*-*N*,*N*,*N'*,*N'*-Tetramethyl-4-cyclohexene-1,2-bis(dimethylamine) (10).** To a suspension of lithium aluminum hydride (31.1 g, 0.82 mol) in anhydrous ether (900 mL) was added a solution of diamide **9** (140.5 g, 0.63 mol) in dry tetrahydrofuran (350 mL) at a rate which maintained gentle reflux. The mixture was then refluxed for 1 h and hydrolyzed by the cautious addition of water (31 mL), 15% NaOH solution (31 mL), and finally water (93 mL). The fine, white precipitate which formed was filtered off, washed with ether (four 200-mL portions), and discarded. The filtrate was concentrated and the residue distilled to give 112.5 g (90%) of diamine **10**: bp 106–109 °C (8 mm); ^1H NMR (CCl_4) δ 1.78–2.48 (complex, 22 H, CH_2, CH, NCH_3), 5.68 (s, 2 H, C=CH).

Anal. Calcd for $C_{12}H_{24}N_2$: C, 73.41; H, 12.32; N, 14.27. Found: C, 73.67; H, 12.49; N, 14.15.

4,5-Dimethylenecyclohexene (1). The general procedure of Cope and Ciganek[15] was followed. To a solution of diamine **10** (96.2 g, 0.49 mol) in methanol (167.0 mL) at 0 °C was added hydrogen peroxide (111.1 mL of a 30% solution, 0.98 mol), followed by additional portions of 111.1 mL each at elapsed times of 3 and 5 h. The resulting solution was stirred for 36 h at room temperature after which a negative phenolphthalein test for basicity was obtained. The excess peroxide was destroyed by stirring the reaction mixture with 100 mg of platinum-on-carbon until the evolution of oxygen ceased (24 h). The catalyst was removed by filtration and the filtrate was concentrated at 50–60 °C by using a rotary evaporator at aspirator pressure, followed by evacuation at 0.1 mm, to give the crude amine oxide as a clear, highly viscous, pale yellow oil. Hydroquinone (0.5 g) was added and the resulting mixture was heated in an oil bath at 150–170 °C (100 mm). The pyrolysate was passed through a water-cooled condenser and then collected in a dry ice–acetone trap. Water (75 mL) was added to the pyrolysate, and the two layers were separated. The upper layer of diene **1** was washed with water (two 25-mL portions), cold 5% HCl (25 mL), saturated $NaHCO_3$ (25 mL), and saturated NaCl (25 mL). The neat diene was dried over anhydrous K_2CO_3 followed by 4A molecular sieves, and filtered through glass wool to give 25.9 g (50%) of **1**, used directly in the cycloadditions. A sample had bp 73–74 °C (85 mm) (lit.[7] bp 90 °C (100 mm)).

2-Phenyl-1,3,4,7-tetrahydroisophosphindole 2-Oxide (2). A general procedure for the cycloaddition follows. Phenylphosphonous dibromide (80.4 g, 0.30 mol) was added to a mixture of 4,5-dimethylenecyclohexene (29.2 g, 0.27 mol) and copper stearate (400 mg) in ligroin (95–105 °C, 150 mL) in a wide-mouthed brown bottle with a Teflon-lined cap. The bottle was loosely capped until the initial exothermic reaction had subsided. As the solid cycloadduct formed, additional solvent was added (three 25-mL portions) to keep the adduct covered. The bottle was tightly sealed and allowed to stand for 5 days. The solid cycloadduct was filtered off, washed with petroleum ether (three 50-mL portions), and added cautiously to an ice-cold saturated $NaHCO_3$ solution (200 mL), forming an insoluble oil. The resulting mixture was then extracted with six 100-mL portions of chloroform. The $CHCl_3$ extract was dried ($MgSO_4$), filtered, and concentrated to give a brown solid residue. Distillation gave 53.1

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[8] L. D. Quin, J. Leimert, E. D. Middlemas, R. W. Miller, and A. T. McPhail, *J. Org. Chem.*, in press.

[9] T. H. Chan and K. T. Nwe, *Phosphorus*, **3**, 225 (1974).

[10] C. N. Robinson and R. C. Lewis, *J. Heterocycl. Chem.*, **10**, 395 (1973).

[11] Melting points were taken on a Mel-Temp apparatus and are corrected. Elemental analyses were performed by MHW Laboratories. ^1H NMR spectra were taken with a JEOL MH-100 spectrometer. ^{31}P NMR spectra (FT) were obtained with a Bruker HFX-10 system at 36.43 MHz with proton noise decoupling; positive chemical shifts are downfield from 85% H_3PO_4 as reference. ^{13}C NMR spectra (FT) were obtained with a JEOL FX-60 spectrometer at 15 MHz with proton noise decoupling; Me_4Si was used as reference.

[12] V. Mark, *Org. Synth.*, **46**, 42 (1966).

[13] H. Schindlbauer and S. Fischer, *Synthesis*, 634 (1972), report a synthesis that does not clearly specify if the product is cis or trans. The reported melting point (41–42.5 °C) does not agree with our value (72–73 °C) or that reported for the trans isomer (55–56 °C[14]).

[14] D. S. Tarbell and B. Wargotz, *J. Am. Chem. Soc.*, **76**, 5761 (1954).

[15] A. C. Cope and E. Ciganek, *Org. Synth.*, **39**, 40 (1959).

Table I. ^{13}C NMR Data[a]

	C-1,3	C-3a,7a	C-4,7	C-5,6	PCH_3
2	38.2 (68.4)	128.8 (9.2)[b]	29.4 (14.0)	123.9 (s)	*c*
3	36.8 (67.1)	127.9 (10.4)	29.3 (13.4)	123.8 (1.8)	16.2 (64.1)
4	34.5 (90.9)	127.3 (13.4)	28.7 (16.5)	123.9 (1.8)	
5	35.4 (67.8)	135.6 (9.8)	127.3 (17.1)[d]	127.8 (s)	*e*
6	34.5 (65.9)	135.0 (10.4)	127.4 (11.6)	127.8 (s)	14.5 (64.7)

[a] $CDCl_3$ solutions except **4** (Me_2SO-d_6). Chemical shifts (parts per million) are downfield from internal Me_4Si Values in parentheses are ^{31}P–^{13}C coupling constants, in hertz. [b] Assignment uncertain. [c] Phenyl signals: ipso, 134.3 (92.8); ortho, 129.8 (9.1);[b] meta, 128.9 (12.2);[b] para, 132.1 (3.0). [d] Downfield signal assumed to be merged with C-5,6. [e] Phenyl signals: ipso, 133.0 (92.2);[f] ortho, 129.7 (9.2); meta, 128.6 (11.6); para, 132.0 (3.1). [f] Upfield signal assumed to be merged with signal of ortho.

g (85%) of phospholene oxide **2** as a colorless oil, bp 154–160 °C (0.02 mm), which quickly solidified to a white solid, mp 109–114 °C. Recrystallization from benzene–ligroin gave white plates: mp 120–121 °C; ^1H NMR ($CDCl_3$) δ 2.32–3.16 (m, 8 H, CH_2), 5.71 (s, 2 H, C=CH), 7.20–7.96 (m, 5 H, phenyl H); ^{31}P NMR ($CDCl_3$) δ +49.7; ^{13}C NMR, Table I.

Anal. Calcd for $C_{14}H_{15}OP$: C, 73.03; H, 6.57; P, 13.45. Found: C, 73.22; H, 6.48; P, 13.81.

2-Methyl-1,3,4,7-tetrahydroisophosphindole 2-Oxide (3). Via the general procedure, a reaction mixture containing methylphosphonous dichloride (17.6 g, 0.15 mol), 4,5-dimethylenecyclohexene (12.9 g, 0.12 mol), copper stearate (150 mg), and ligroin (150 mL) was allowed to stand for 25 days. Distillation of the hydrolyzed product (recovered by continuous extraction with $CHCl_3$ for 48 h) gave 18.1 g (92%) of phospholene oxide **3** as a colorless oil, bp 119–124 °C (0.02 mm), which quickly solidified to a white, hygroscopic solid: mp 107–110 °C; ^1H NMR ($CDCl_3$) δ 1.70 (d, $^2J_{PH}$ = 14 Hz, PCH_3), 2.13–2.96 (m, 8 H, CH_2), 5.77 (s, 2 H, C=CH); ^{31}P NMR ($CDCl_3$) +58.1 (D_2O), +68.9; ^{13}C NMR, Table I.

Anal. Calcd for $C_9H_{13}OP$: C, 64.28; H, 7.79; P, 18.42. Found: C, 64.48; H, 7.96; P, 18.45.

2-Hydroxy-1,3,4,7-tetrahydroisophosphindole 2-Oxide (4). Via the general procedure, a reaction mixture containing phosphorus tribromide (40.6 g, 0.15 mol), 4,5-dimethylenecyclohexene (12.9 g, 0.12 mol), copper stearate (150 mg), and ligroin (150 mL) gave after 10 days 15.9 g (78%) of phosphinic acid **4** as a tan solid; mp 181–188 °C. Recrystallization from absolute ethanol gave white needles: mp 189–192 °C; ^1H NMR (Me_2SO-d_6) δ 2.27 (d, $^2J_{PH}$ = 12 Hz, 4 H, PCH_2), 2.64 (s, 4 H, CH_2), 5.72 (s, 2 H, C=CH), 7.76 (br s, 1 H, OH); ^{31}P NMR (Me_2SO-d_6) δ +60.1; ^{13}C NMR, Table I.

Anal. Calcd for $C_8H_{11}O_2P$: C, 56.47; H, 6.52; P, 18.20. Found: C, 56.31; H, 6.26; P, 17.96.

2-Phenylisophosphindoline 2-Oxide (5). To a solution of phospholene oxide **2** (1.7 g, 7.4 mmol) in anhydrous benzene (65 mL) was added DDQ (1.8 g, 8.1 mmol), and the resulting solution was refluxed for 18 h. The reaction mixture was cooled and the precipitated hydroquinone was filtered off and washed with benzene (three 25-mL portions). The filtrate was then washed with 1% NaOH (three 25-mL portions), and the base washes were extracted with benzene (four 25-mL portions). The benzene solutions were combined, dried ($MgSO_4$), and concentrated to give 0.85 g (47%) of the monohydrate of **5** as a white solid: mp 99–102 °C (lit.[9] mp for the monohydrate, 98–100 °C); ^{13}C NMR, Table I.

2-Methylisophosphindoline 2-Oxide (6). To a suspension of phospholene oxide **3** (2.0 g, 11.9 mmol) in 100 mL of anhydrous benzene was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (3.0 g, 13.1 mmol). The resulting mixture was refluxed for 18 h. The precipitated hydroquinone was filtered off and washed with benzene (three 50-mL portions). The filtrates were concentrated to give a dark brown solid residue. A 1% NaOH solution (50 mL) was added to the residue and the resulting solution was extracted continuously for 48 h with chloroform. The chloroform extract was dried ($MgSO_4$), filtered, and concentrated at reduced pressure (finally 0.1 mm) to give a yellow solid. Kugelrohr distillation (120 °C (0.02 mm)) gave 1.3 g (66%) of the phosphindoline oxide **6** as a colorless oil which solidified on standing to a white, hygroscopic solid: mp 84–86 °C; ^1H NMR ($CDCl_3$) δ 1.59 (d, $^2J_{PH}$ = 13 Hz, PCH_3), 2.86–3.53 (m, 4 H, CH_2), 7.22 (s, 4 H, C=CH); ^{31}P NMR (D_2O) δ +73.3; ^{13}C NMR, Table I.

Anal. Calcd for $C_9H_{11}OP$: C, 65.06; H, 6.67; P, 18.64. Found: C, 65.34; H, 6.83; P, 18.47.

2-Hydroxyisophosphindoline 2-Oxide (7). To a suspension of phosphinic acid **4** (2.0 g, 11.8 mmol) in anhydrous benzene (100 mL) was added DDQ (3.0 g, 13.0 mmol), and the resulting mixture was refluxed for 18 h. The precipitated hydroquinone was filtered off and washed with benzene (three 25-mL portions). The filtrate was then concentrated to give a dark brown solid which was washed with ethyl acetate (three 25-mL portions) to give 1.8 g (91%) of isophosphindoline **7** as a tan solid; mp 154–157 °C. Recrystallization from water gave white needles; ^{31}P NMR ($CDCl_3$) δ +71.2. Since the melting point (156–158 °C) did not match the literature value (142–148 °C[4d]), analysis was performed.

Anal. Calcd for $C_8H_9O_2P$: C, 57.15; H, 5.40; P, 18.42. Found: C, 57.41; H, 5.25; P, 18.63.

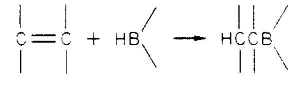
Registry No. 1, 54290-41-4; **2**, 70179-63-4; **3**, 70179-64-5; **4**, 70179-65-6; **5**, 50869-62-0; **6**, 70179-66-7; **7**, 20148-17-8; **8**, 2305-26-2; **9**, 70179-67-8; **10**, 70179-68-9; phenylphosphonous dibromide, 1073-47-8; methylphosphonous dichloride, 676-83-5; phosphorus tribromide, 7789-60-8; *cis*-*N*,*N*,*N'*,*N'*-tetramethyl-4-cyclohexene-1,2-bis(dimethylamine) *N*,*N'*-dioxide, 70179-61-2.

Communications

Unusual Kinetics for the Hydroboration of Alkenes with 9-Borabicyclo[3.3.1]nonane

Summary: Kinetics of the reaction of dimeric 9-borabicyclo[3.3.1]nonane with representative alkenes establishes that hydroboration proceeds through prior dissociation of the dimer into monomer, leading to simplified kinetic expressions, $k_1[(9\text{-BBN})_2]$ for reactive alkenes and $k_{3/2}[(9\text{-BBN})_2]^{1/2}$ [alkene] for less reactive alkenes.

Sir: Hydroboration is a remarkably clean reaction broadly applicable to almost the entire range of unsaturated organic structures[1-3] (eq 1). The addition of the HB< bond



$$\text{C}{=}\text{C} + \text{HB}\langle \longrightarrow \text{HCCB}\langle \qquad (1)$$

to the carbon–carbon double bond is cleanly cis.[4] The reaction has been proposed to proceed through a facile 2